MEASUREMENT OF POLYCYCLIC AROMATIC HYDROCARBONS IN AIRBORNE PARTICULATE MATTER AT LOW CONCENTRATIONS

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Office of Research and Development
US Environmental Protection Agency

Report Documentation Page

Form Approved
OMB No. 0704-0188

1. REPORT DATE	2. REPORT TYPE	3. DATES COVERED
MAR 2012		**00-00-2012 to 00-00-2012**

4. TITLE AND SUBTITLE	5a. CONTRACT NUMBER
Measurement of Polycyclic Aromatic Hydrocarbons in Airborne Particulate Matter at Low Concentrations	5b. GRANT NUMBER
	5c. PROGRAM ELEMENT NUMBER
6. AUTHOR(S)	5d. PROJECT NUMBER
	5e. TASK NUMBER
	5f. WORK UNIT NUMBER
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) **US Environmental Protection Agency,National Center for Environmental Assessment,Two Potomac Yard 2733 South Crystal Dr,Arlington,VA,22202**	8. PERFORMING ORGANIZATION REPORT NUMBER
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)	10. SPONSOR/MONITOR'S ACRONYM(S)
	11. SPONSOR/MONITOR'S REPORT NUMBER(S)

12. DISTRIBUTION/AVAILABILITY STATEMENT
Approved for public release; distribution unlimited

13. SUPPLEMENTARY NOTES
Presented at the 9th Annual DoD Environmental Monitoring and Data Quality (EDMQ) Workshop Held 26-29 March 2012 in La Jolla, CA.

14. ABSTRACT

15. SUBJECT TERMS

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT **unclassified**	b. ABSTRACT **unclassified**	c. THIS PAGE **unclassified**	**Same as Report (SAR)**	**37**	

EPA Methods for Species of Greatest Concern

http://www.epa.gov/osw/hazard/testmethods/sw846/online/
(Chapter 2 = Choosing the Correct Procedure)

010-100 – air (mostly emissions)
200 Series – inorganics in drinking water
500 Series – organics in drinking water
600 Series – organics in wastewater
1600 Series – “clean methods” (?)
3000 Series – digestion methods for metals
3500 Series – organic extraction methods
3600 Series – organic cleanup methods
5000 Series – VOC preparation for solid waste
7000 Series – atomic absorption methods (+ others?)
8000 Series – organic analysis
TO air toxics (not in sw846)

1,4-Dioxane

- 8260 VOC's by GCMS (often used with purge & trap)
- 8270 Extraction/GCMS
- 8015 Non-halogenated semi-volatiles by GC
- 5030 Purging at Elevated Temperature
- 5031 Azeotropic Distillation
- 624 VOC's by GCMS
- 625 Semi-Volatiles by GCMS
- TO-15 VOC's/canisters

Trichloroethylene

- 8010 Halogenated hydrocarbons by GC
- 8021B Aromatics & Halogens by photoionization
- 8260B VOC's by GCMS (e.g., after purge & trap)
- 524.2 Purgeable Organics by GCMS
- 601,602 Purgeable Aromatics & Halocarbons
- 624 VOC's by GCMS
- TO-15 VOC's/canisters

Dioxins

23	Stationary Source Sampling
1613	GCMS wastewater
8280, 8290	GCMS method specifically for dioxins
TO-9A with high volume PUF sampler: Ferrario et al Organohalogen Compounds 50, 35-39	

Hexavalent Chromium

3060	Alkaline digestion
7196A	Soil & Water Colorimetric (diphenylcarbazide)
7199	Hexavalent Chromium by Ion Chromatography
218.6	Low level chelation & extraction
NATTS	Technical Assistance Document for NATTS Collection on $NaHCO_3$ impreganted cellulose filters Analysis by IC (www.epa.gov/ttnamti1/airtox.html)

Polycyclic Aromatic Hydrocarbons

8270C – GCMS
8272 – SPME-GCMS-SIM
8310 – HPLC
550.1 – HPLC (drinking water)

3500 – Organic Extraction
3545 – Pressurized Fluid Extraction

3535 – Solid Phase Extraction

TO-13A

RESEARCH: PM ORGANIC TARGET COMPOUNDS

n-Alkanes: C23 to C34

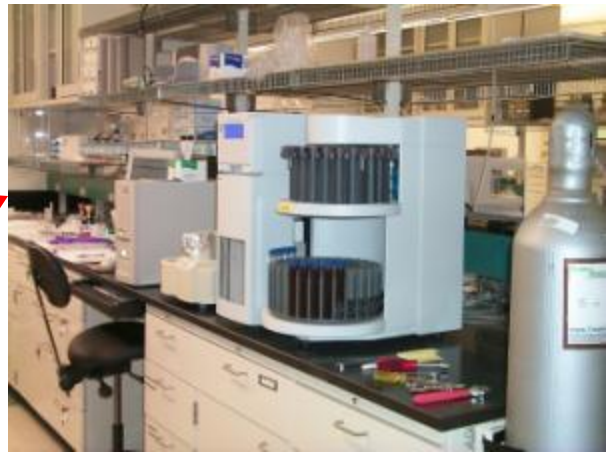
Polycyclic aromatic hydrocarbons: pyrene, chrysene, benzofluoranthenes, benzo[a]pyrene, indeno[1,2,3-cd]pyrene, benzo[ghi]perylene

Hopanes: norhopane, hopane, homohopane

Aliphatic Acids: C16, C18, C16:1, C18:1
Levoglucosan

Sample Collection
113 Liters/Min
Quartz Fiber Filters
Tisch TE-1202 Sampler

Sample Extraction
Pressurized Solvent Extraction
1:1:1 Hexane:Dichloromethane:Methanol
Dionex ASE 200



Sample Concentration
Evaporation in Ultrapure Nitrogen Stream
Zymark Turbovap

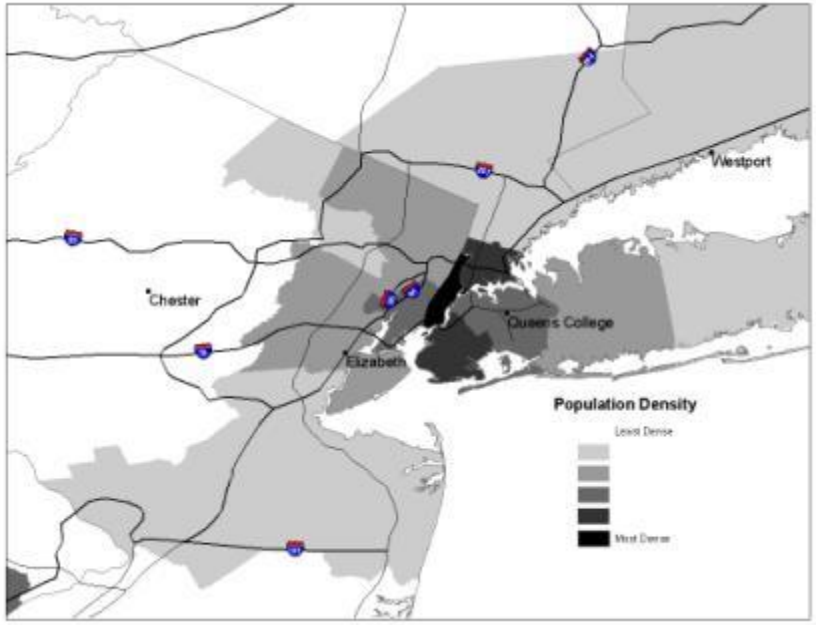
Solid Phase Extraction
Supelco Custom Glass Silica SPE Cartridge
1% Dichloromethane + 1% Acetone in Hexane

GCMS Analysis
Conventional Splitless Injection
Selective Ion Monitoring
DB-5MS Column

www.epa.gov/airscience

A REGIONAL SAMPLING NETWORK FOR SPECIATION OF ORGANICS IN PM-2.5 IN THE NEW YORK CITY AREA

Steve McDow & Min Li - Drexel University
Monica Mazurek - Rutgers University
Lee Alter & John Graham - NESCAUM
Dirk Felton - NY DEC
Tom McKenna & Charlie Pietarinen - NJ DEP
Al Leston - Connecticut DEP



OBJECTIVES

- Collect enough sample to analyze
- Low blank levels

R&P
Partisol 2300

APPROACH

Use extra
Channel from speciation samplers and analyze 47 mm quartz filter composites by GCMS

Met One SASS

PRELIMINARY FIELD TEST

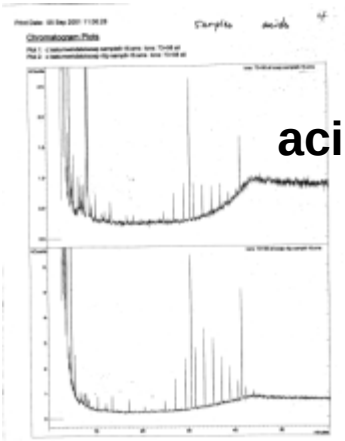
Insufficient Sample Collection:

- *n*-alkanes C22-C28 concentration ~ 10 to 50 ng/m^3
- 2 hopanes barely detectable
- PAH's not detected

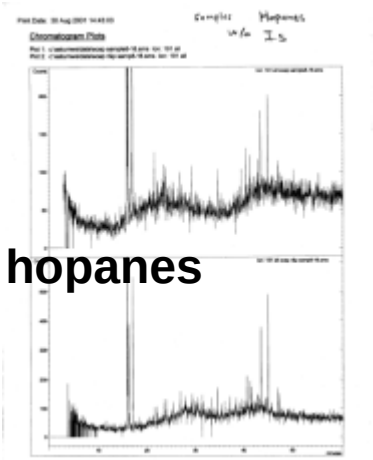
High Blanks

- n-alkane blank levels ~ 5 to 20% of sample concentrations
- hopanes also detectable in blanks

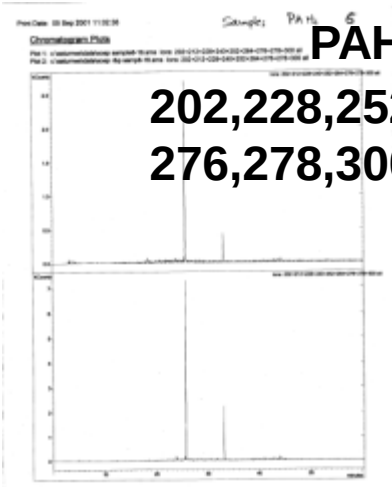
alkanes



acids



hopanes



PAHs
202,228,252
276,278,300

Corrective Action:

- **Increase flow rate**
- **Increase sampling time**

Tisch TE-1202 Sampler

(*Large Volume Injection is another option)

DEARS SAMPLING

Central Site

Residential Monitor

Further Method Development and Improvement

Organic Analysis Challenges	**limited standard reference materials** **missing calibration standards** **non-selective (GCMS not yet developed)** **substantial & variable sample loss in workup** **time & labor intensive procedures**
Required Method Decisions	**can we analyze without cleanup or fractionation?** **internal or external standards?** **how many internal standards?**
Desired Analytical Advances	**5-point calibration curves for all analytes** **submission of methods paper** **recommendation to follow EPA & FDA Methods**

Resources for Development of Quality Assurance Procedures

EPA Forum on Environmental Measurements:
Validation and Peer Review US EPA Chemical Methods of Analysis
www.epa.gov/fem/pdfs/FEM_MV_doc_final_10-14-2005.pdf

Thompson et al. (IUPAC) Harmonized guidelines for single laboratory Validation of methods of analysis Pure Appl Chem 2002 74, 835-855

Eurachem, The Fitness of Purpose of Analytical Methods 1998

International Organization for Standardization, ISO 5275-1

AOAC Official Methods Program Manual, Appendix D:
Guidelines for Collaborative Study Procedures to Validate Characteristics Of a Method of Analysis

Resources for Development of Quality Assurance Procedures

Method 8270C (Semi-Volatiles, including PAHs)
Method 8000C (Determinative Chromatographic Separations)
Method 3500 (Organic Extraction)
SW-846 Chapter 1 (Quality Control)
SW-846 Chapter 4 (Organic Analytes)

METHOD PROFICIENCY DEMONSTRATION

- Acceptable average recovery of matrix spike of certified standard solutions (70-130%) (New NIST standards)
- Acceptable reproducibility of matrix spike of certified standard solutions (all 4 replicates 70-130%)

ON-GOING QA

- Method Detection Limit (3σ for 7 injections at 2 to 5 x MDL)
- 1 Calibration check per batch of <20 samples
- 1 Matrix spike of certified standard solutions per batch of <20 samples
- 1 duplicate sample per batch of < 20 samples
- Check surrogate recoveries for each sample

ACCEPTANCE CRITERIA: all analytes or 80% within 20% of target value?

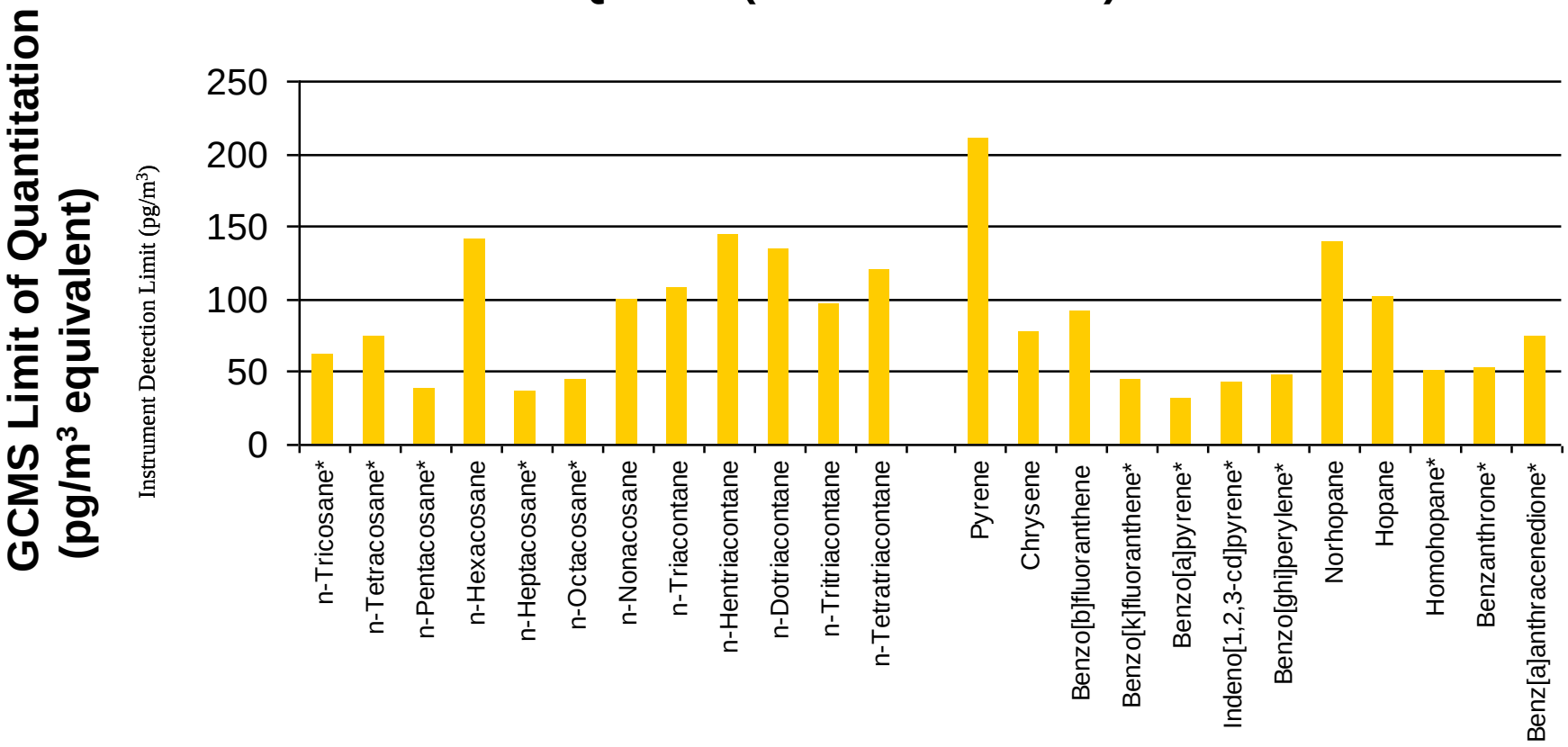
SPIKING LEVEL: 10 to 50 x MDL or typical sample concentration?

Determining Method Detection Limits

1) Prepare standard 1-5 x MDL
2) Analyze at least 7 aliquots
3) Calculate variance (s^2)
4) Calculate MDL for t = n-1, α=0.99 (=3.143s)
5) Verify average is 1 to 5 x MDL
6) Adjust standard concentration and repeat if necessary

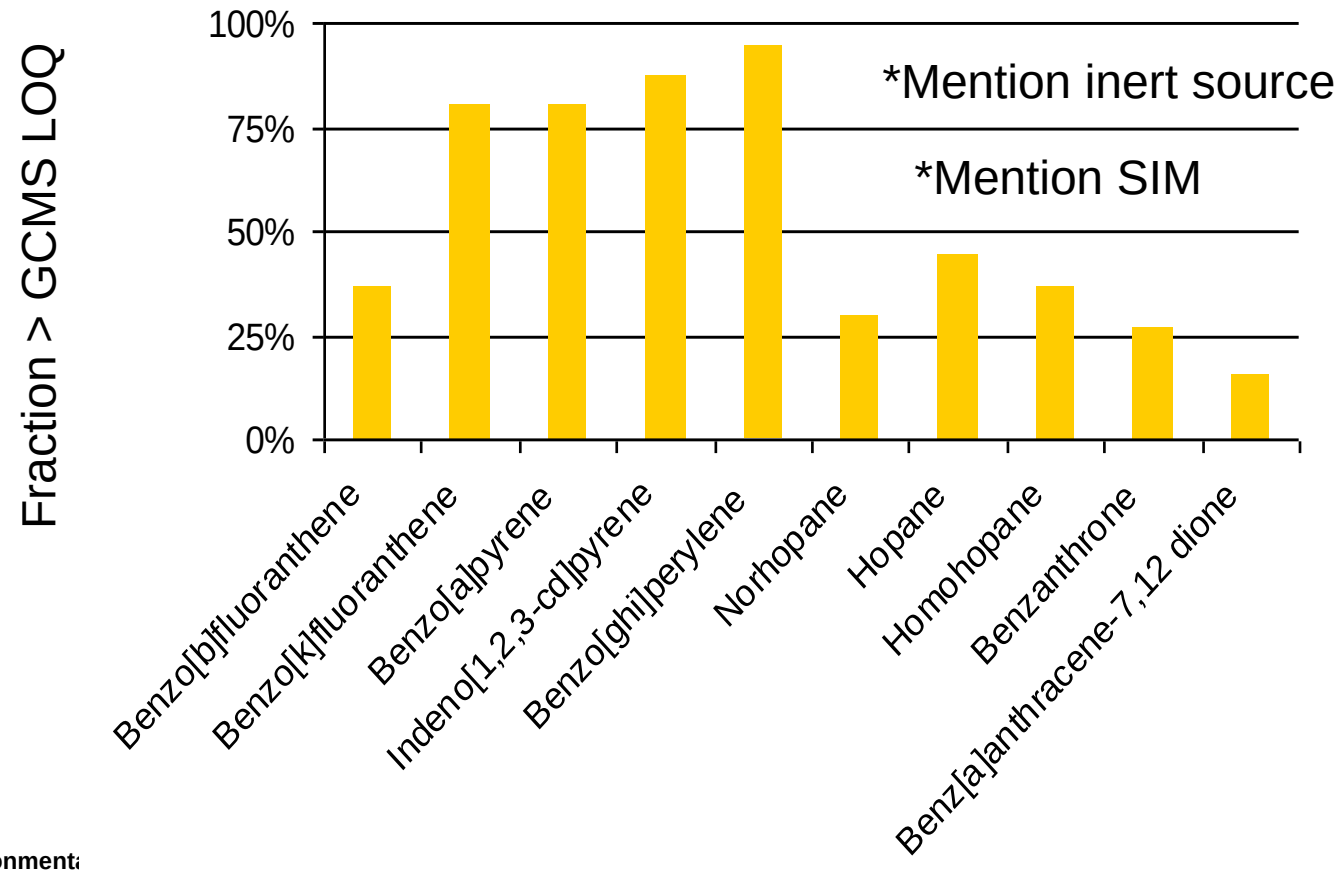
Source: 40CFR136, Appendix B

GCMS Limits of Quantitation
LOQ = 10s (from 40CFR136B)



Fraction of TACS Samples > GCMS LOQ

n =84



Summary of Season 1 High Volume Samples

Analytical blanks – acceptable
Analytical precision – acceptable
Sampling blanks & precision – not evaluated

Calibration frequency – **not acceptable**
> solid phase extract step required
> (extremely low concentrations!)

Surrogate recoveries – **not acceptable**
> collected PM strongly influences surrogate recovery
> internal standards for a range of volatility are necessary
> surrogate standards need to better align with targets

High volume PM samples (DEARS)

- Hexane, methanol, dichloromethane extraction
- Leads to column degradation
- Frequent recalibrations

Low volume PM samples (TACS)

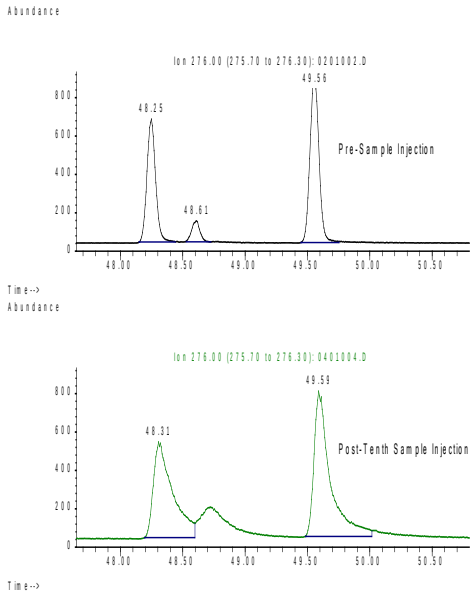
- Pentane, methanol, dichloromethane extraction
- Large volume leads to very severe column degradation (major peak loss)
- Splitless leads to slower column degradation but frequent recalibrations

Non-samples (wet or dry blank quartz filters), Splitless injection

- Hexane, methanol, dichloromethane extraction
- No apparent chromatography issues
- Problems only arise from extraction of real PM samples

Dichloromethane extractions

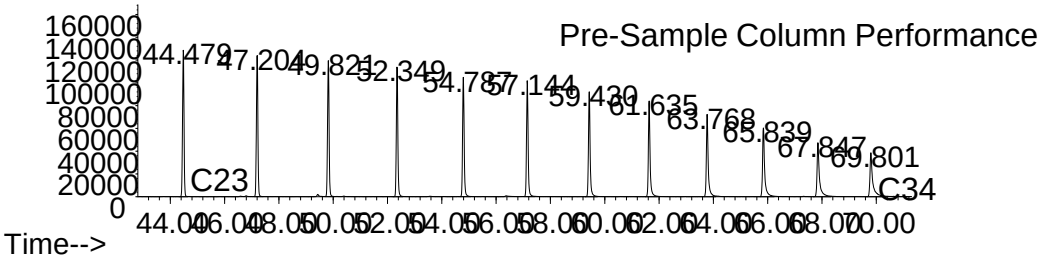
- Degradation slowed but not eliminated

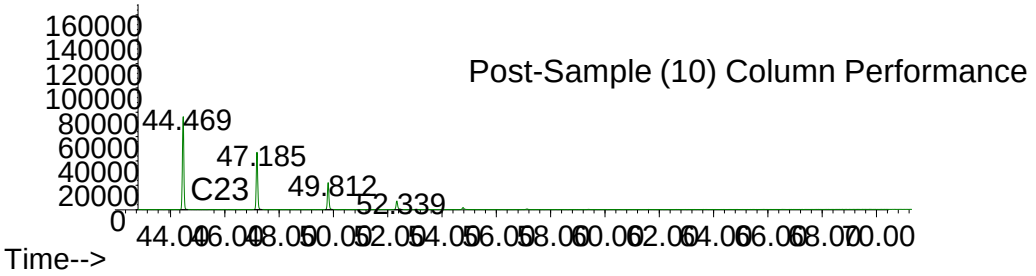


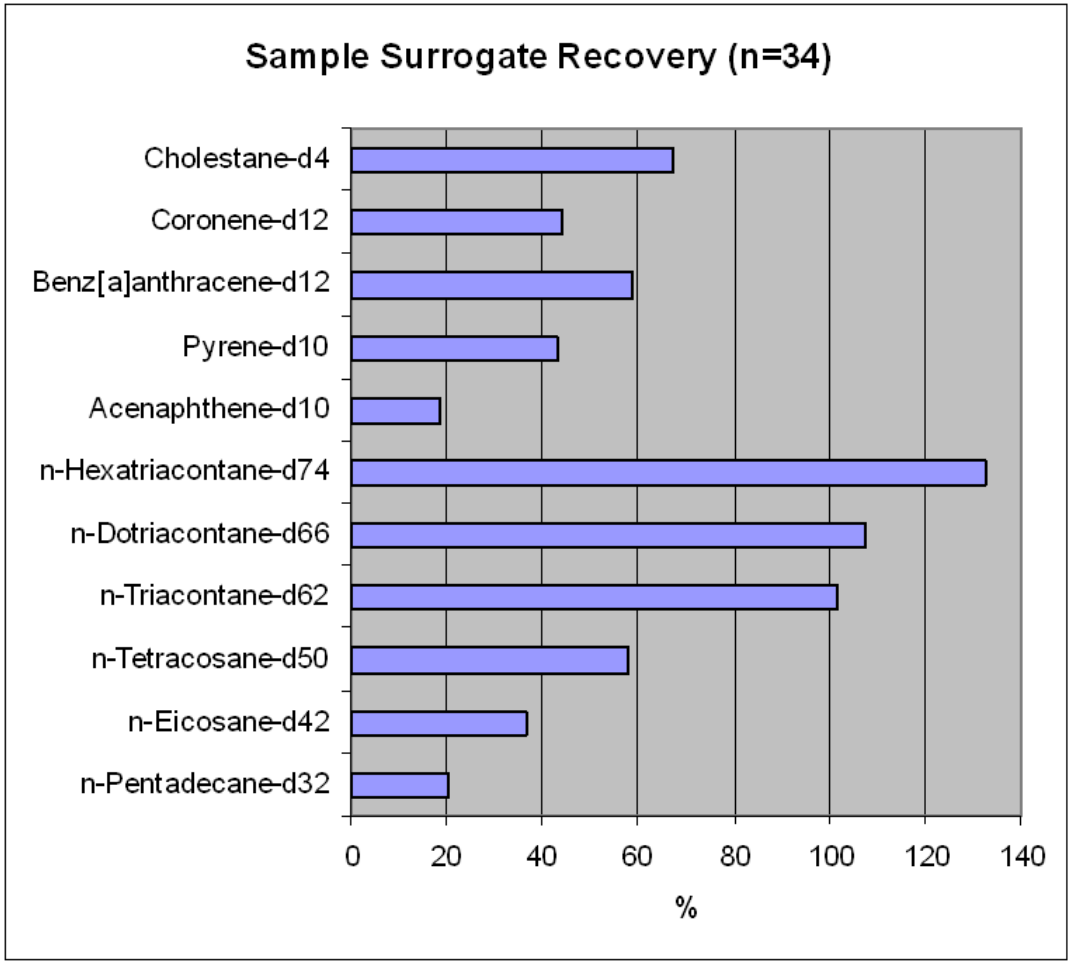
Pre and Post-Sample Column Performance

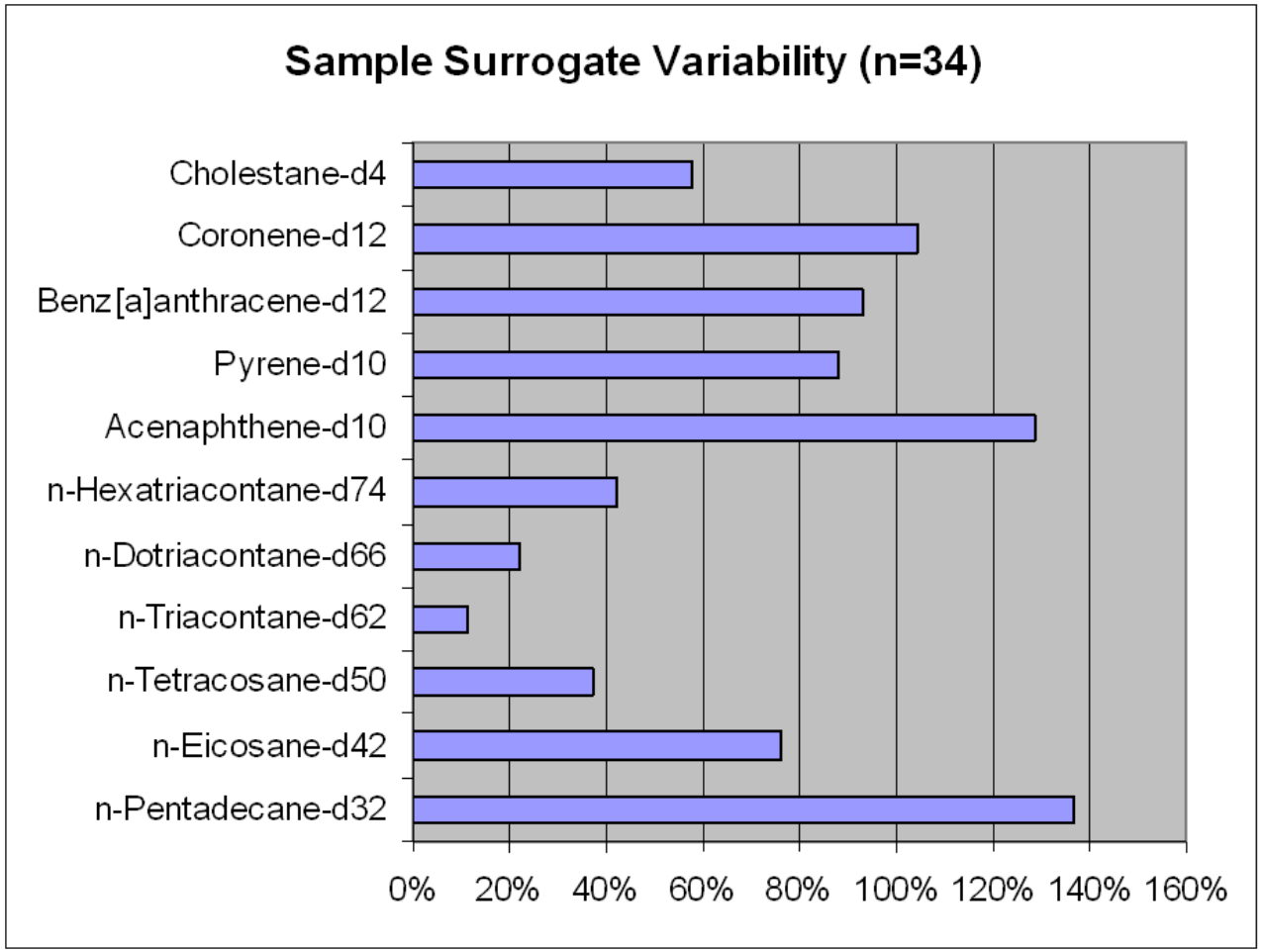
85 TACS samples analyzed

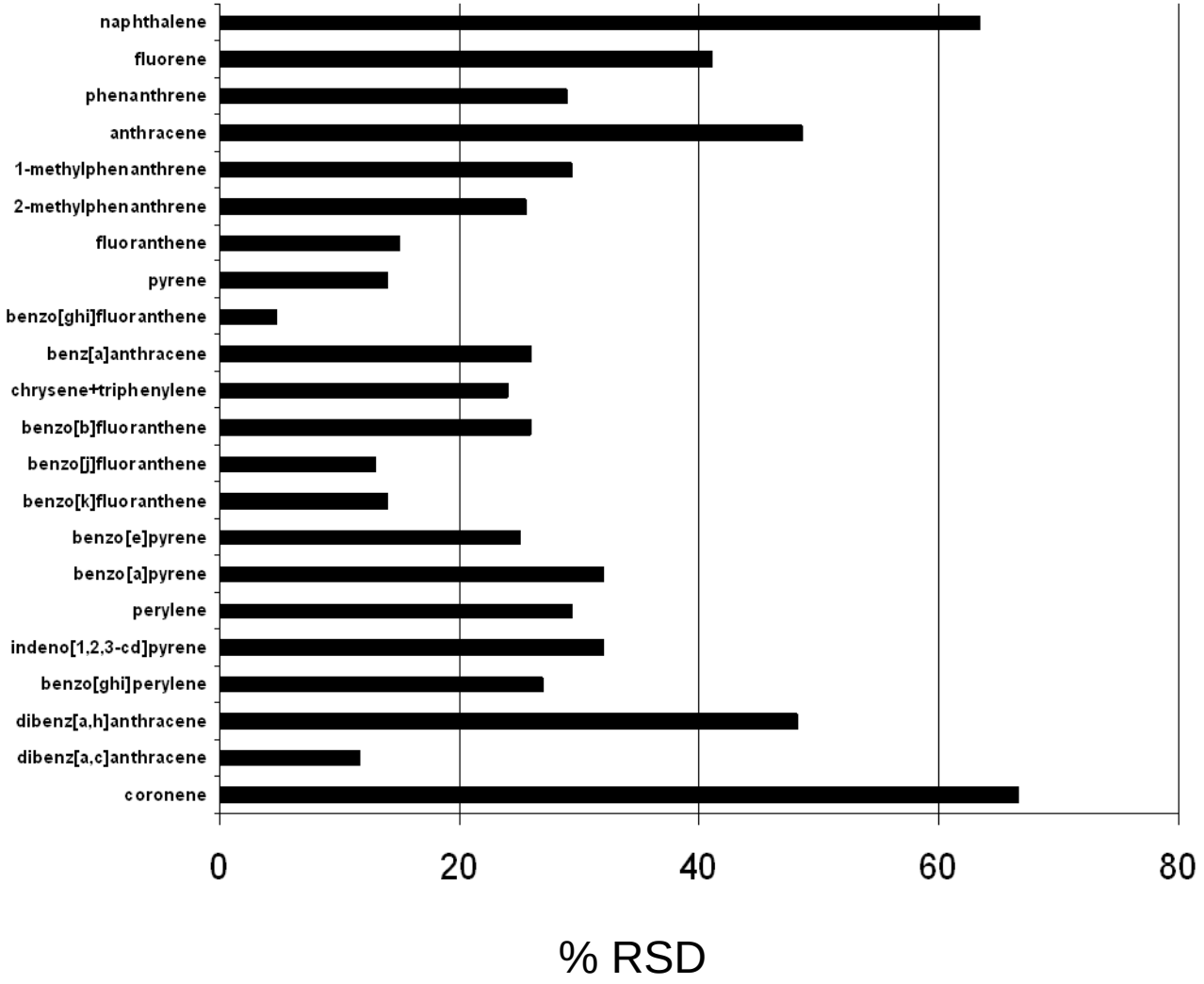
Persistent Column degradation
Frequent recalibration required






Sample Surrogate Recovery (n=34)
Cholestane-d4
Coronene-d12
Benz[a]anthracene-d12
Pyrene-d10
Acenaphthene-d10
n-Hexatriacontane-d74
n-Dotriacontane-d66
n-Triacontane-d62
n-Tetracosane-d50
n-Eicosane-d42
n-Pentadecane-d32
0
20
40
60
80
100
120
140
%


Sample Surrogate Variability (n=34)
Cholestane-d4
Coronene-d12
Benz[a]anthracene-d12
Pyrene-d10
Acenaphthene-d10
n-Hexatriacontane-d74
n-Dotriacontane-d66
n-Triacontane-d62
n-Tetracosane-d50
n-Eicosane-d42
n-Pentadecane-d32
0%
20%
40%
60%
80%
100%
120%
140%
160%

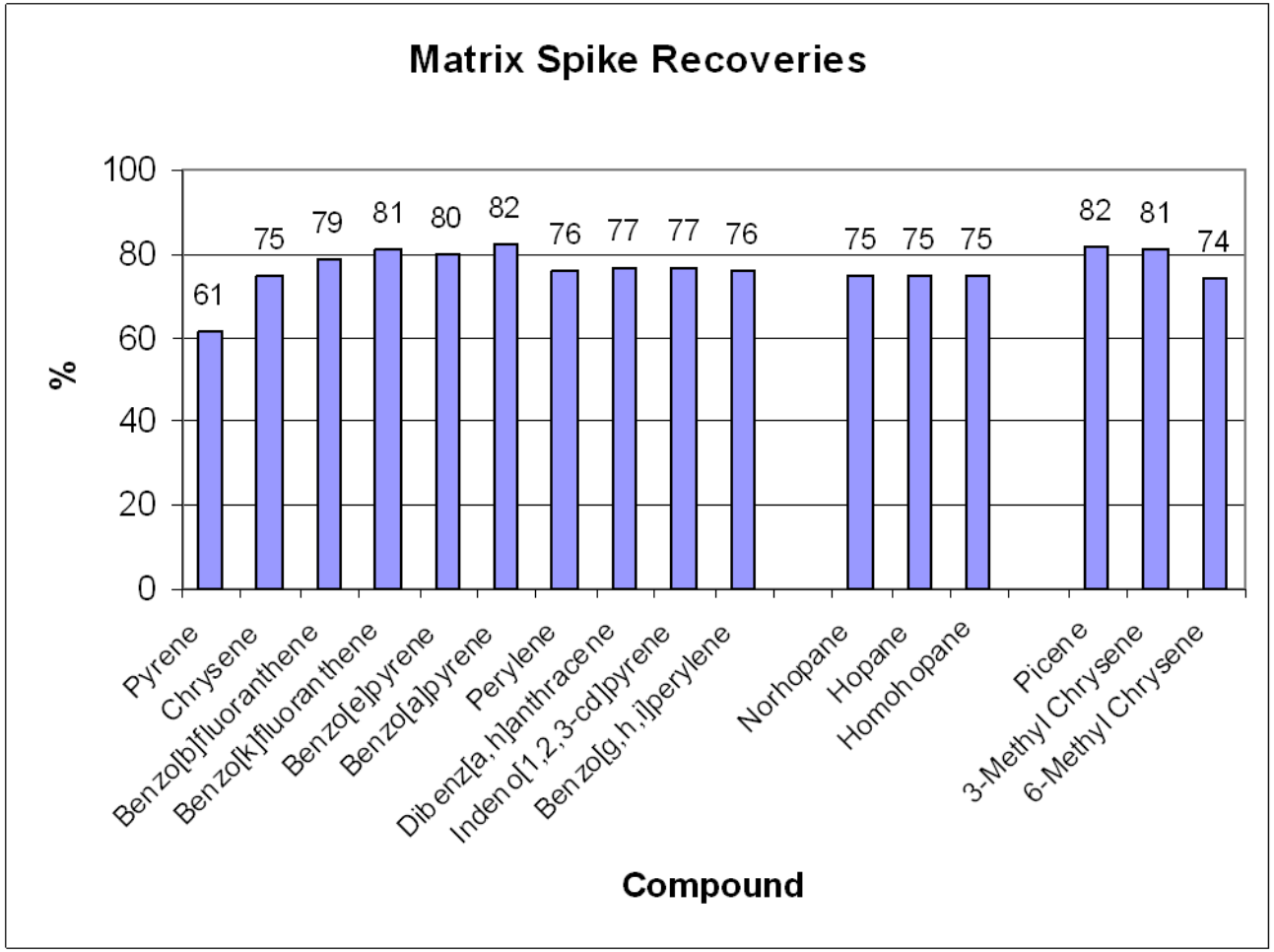

naphthalene
fluorene
phenanthrene
anthracene
1-methylphenanthrene
2-methylphenanthrene
fluoranthene
pyrene
benzo[ghi]fluoranthene
benz[a]anthracene
chrysene+triphenylene
benzo[b]fluoranthene
benzo[j]fluoranthene
benzo[k]fluoranthene
benzo[e]pyrene
benzo[a]pyrene
perylene
indeno[1,2,3-cd]pyrene
benzo[ghi]perylene
dibenz[a,h]anthracene
dibenz[a,c]anthracene
coronene
0
20
40
60
80
% RSD

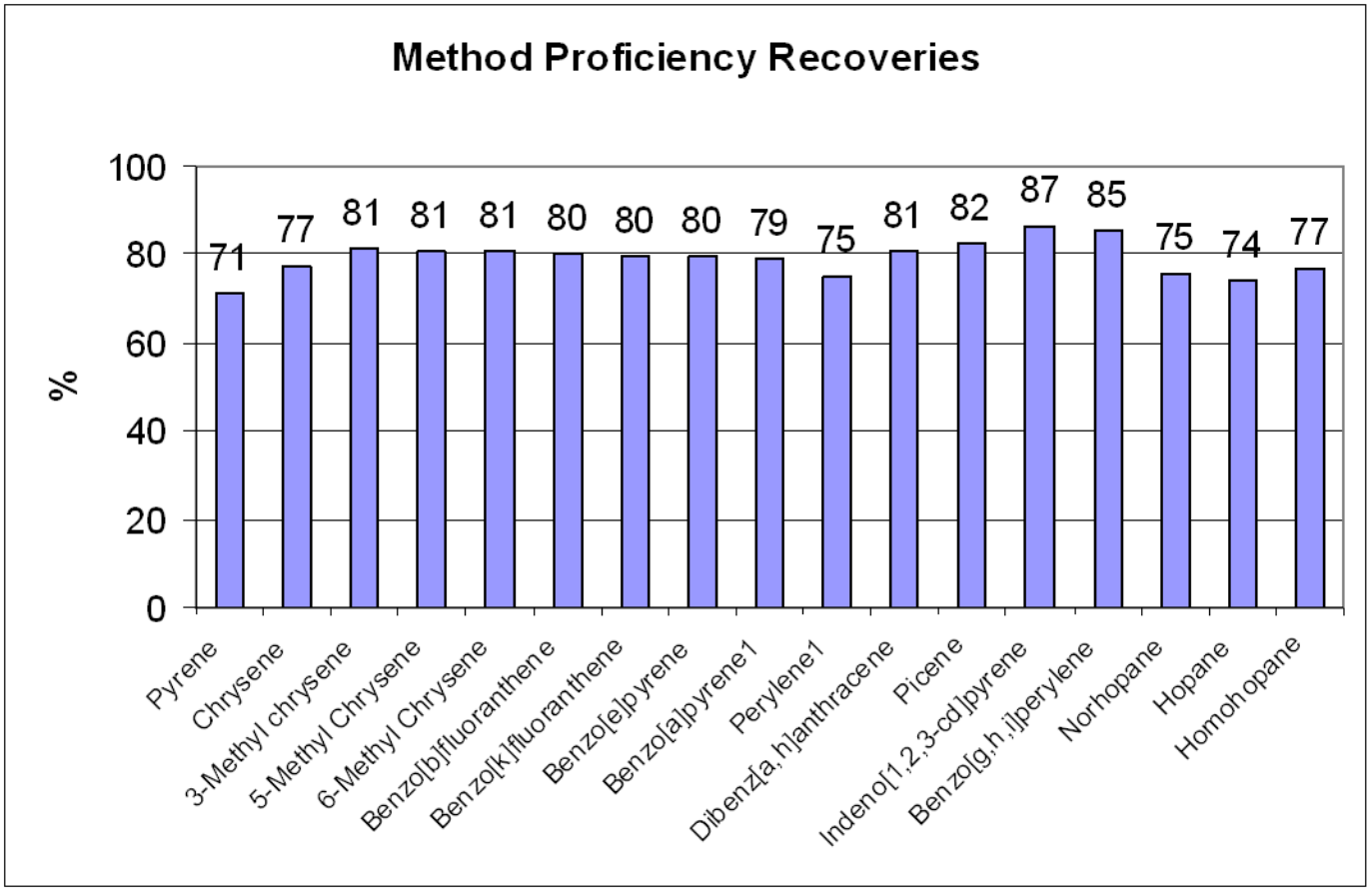
Without Solid Phase Extraction

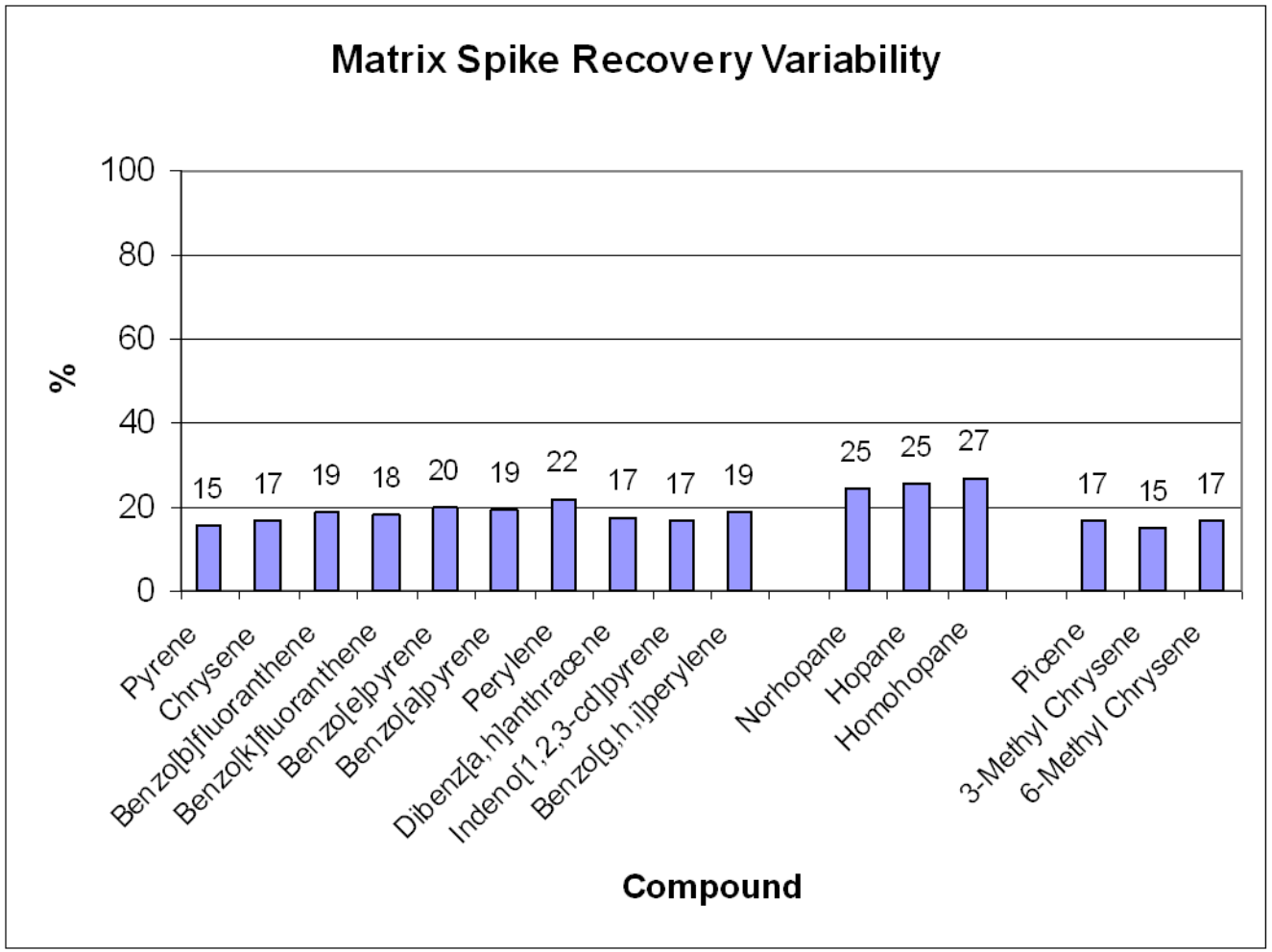
- 2 - 3 samples: Peak shape, calibration suffer
- 30 - 40% deviation from calibration target
- Frequent maintenance, recalibration

With Solid Phase Extraction

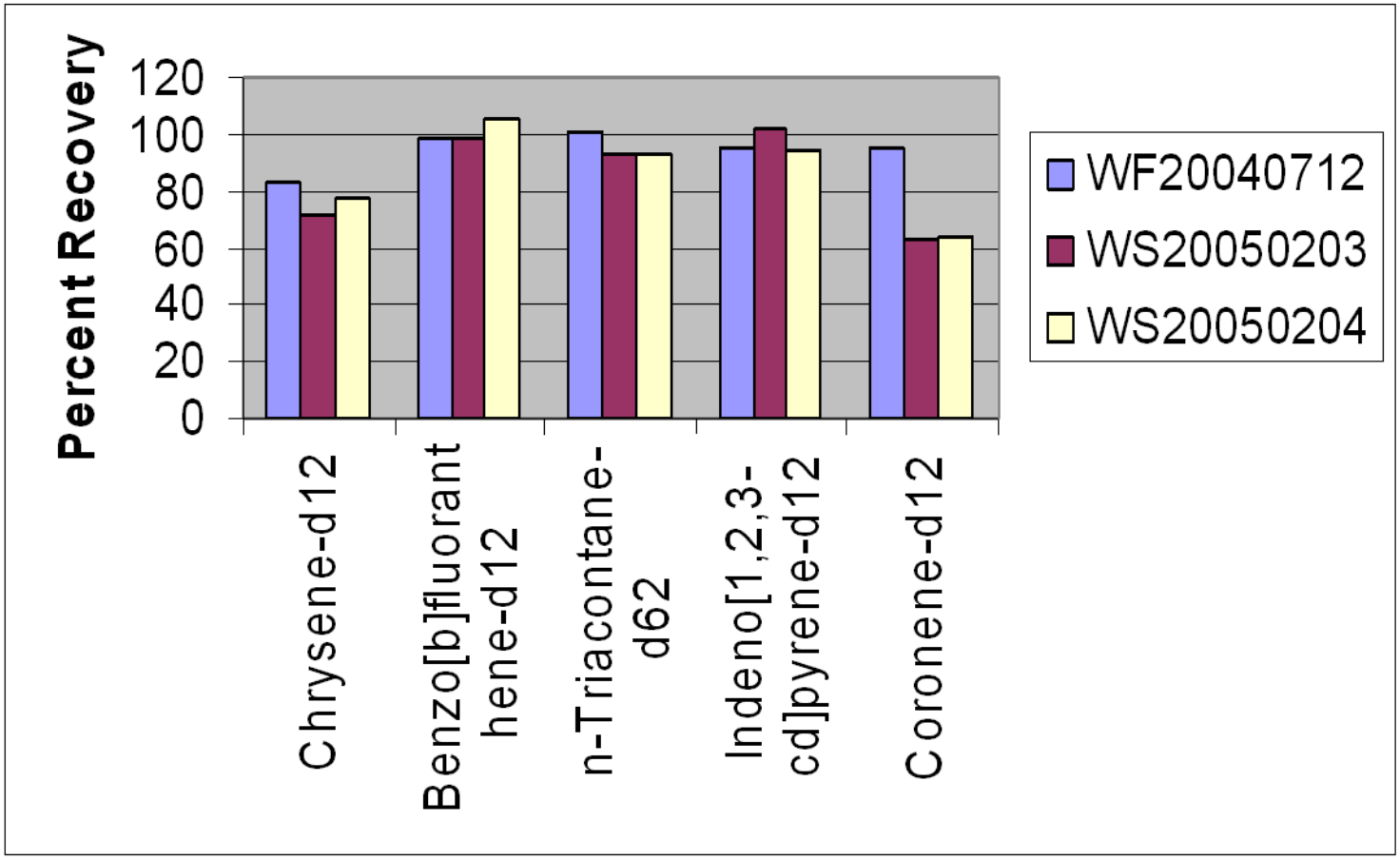
- Noted chromatography/calibration improvement
- Generally < 20% deviation from calibration target

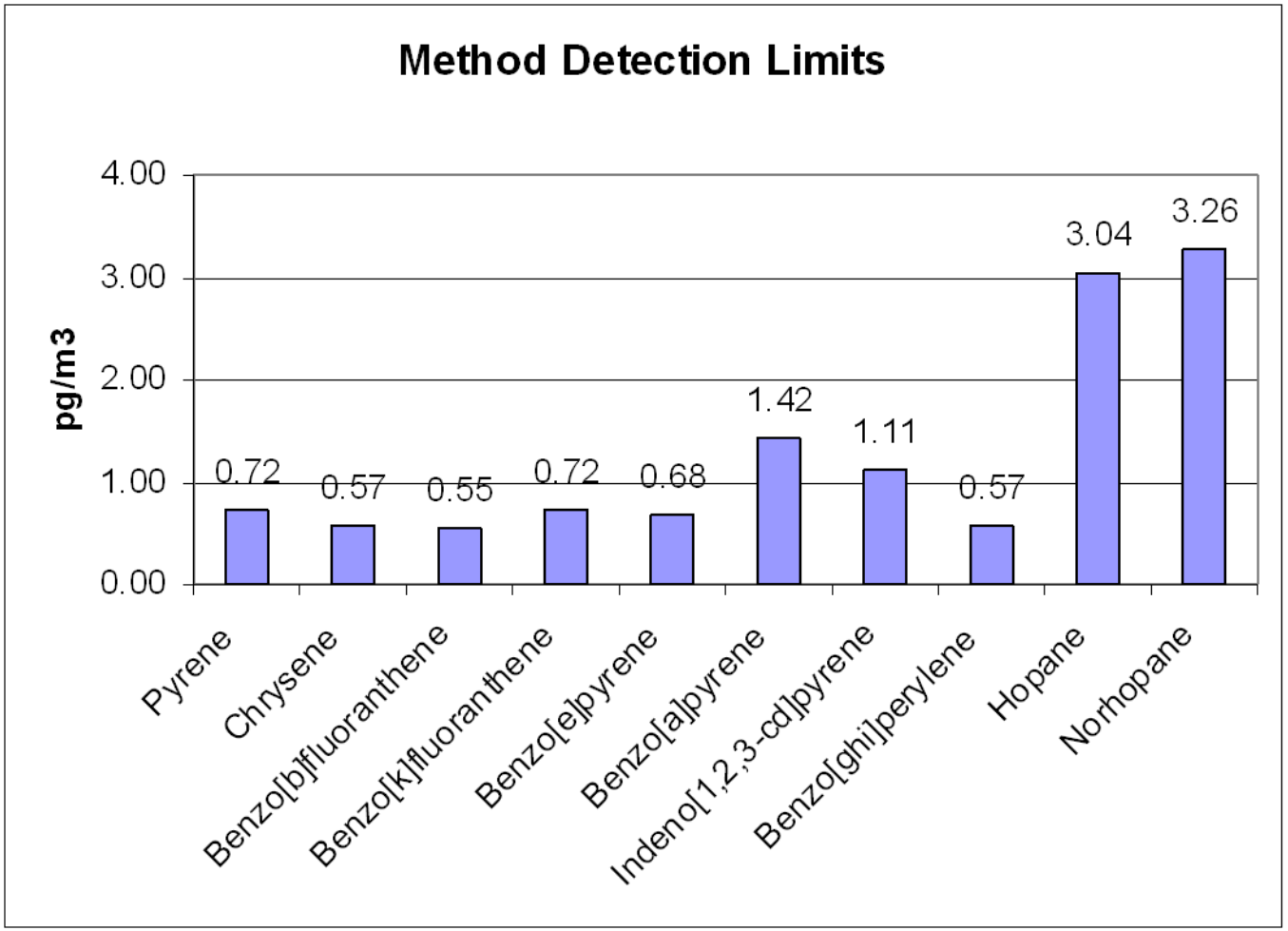

Matrix Spike Recoveries
100
80
60
40
20
0
%
61
75
79
81
80
82
76
77
77
76
75
75
75
82
81
74
Pyrene
Chrysene
Benzo[b]fluoranthene
Benzo[k]fluoranthene
Benzo[e]pyrene
Benzo[a]pyrene
Perylene
Dibenz[a,h]anthracene
Indeno[1,2,3-cd]pyrene
Benzo[g,h,i]perylene
Norhopane
Hopane
Homohopane
Picene
3-Methyl Chrysene
6-Methyl Chrysene
Compound

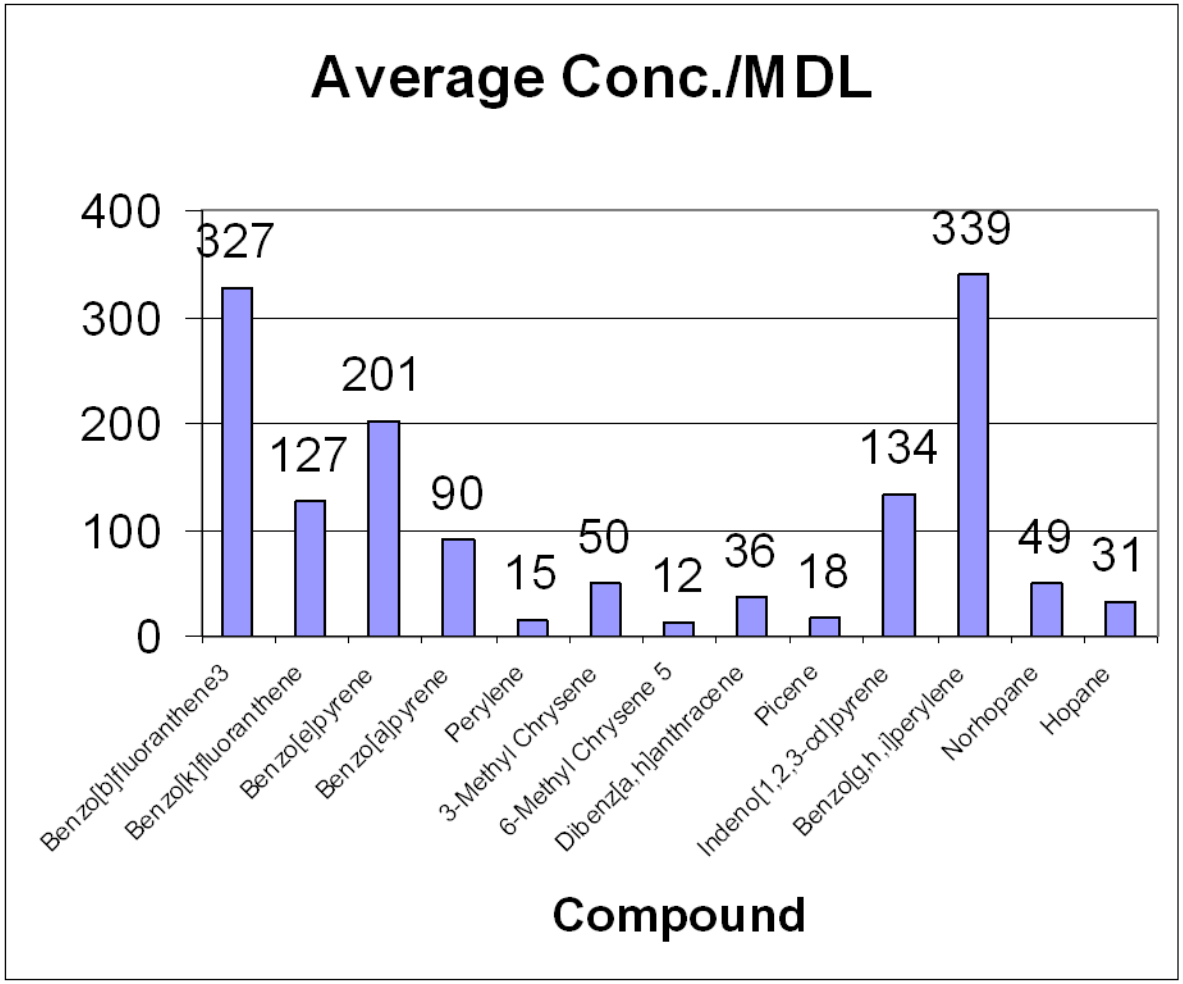

Method Proficiency Recoveries
%
100
80
60
40
20
0
71
77
81
81
81
80
80
80
79
75
81
82
87
85
75
74
77
Pyrene
Chrysene
3-Methyl chrysene
5-Methyl Chrysene
6-Methyl Chrysene
Benzo[b]fluoranthene
Benzo[k]fluoranthene
Benzo[e]pyrene
Benzo[a]pyrene1
Perylene1
Dibenz[a,h]anthracene
Picene
Indeno[1,2,3-cd]pyrene
Benzo[g,h,i]perylene
Norhopane
Hopane
Homohopane


Matrix Spike Recovery Variability
100
80
60
40
20
0
%
15
17
19
18
20
19
22
17
17
19
25
25
27
17
15
17
Pyrene
Chrysene
Benzo[b]fluoranthene
Benzo[k]fluoranthene
Benzo[e]pyrene
Benzo[a]pyrene
Perylene
Dibenz[a,h]anthracene
Indeno[1,2,3-cd]pyrene
Benzo[g,h,i]perylene
Norhopane
Hopane
Homohopane
Picene
3-Methyl Chrysene
6-Methyl Chrysene
Compound

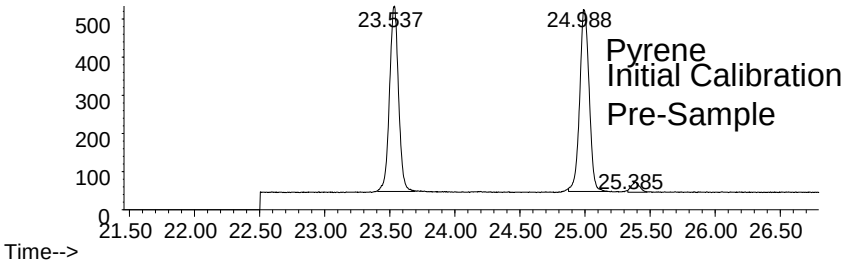
Surrogate Recoveries

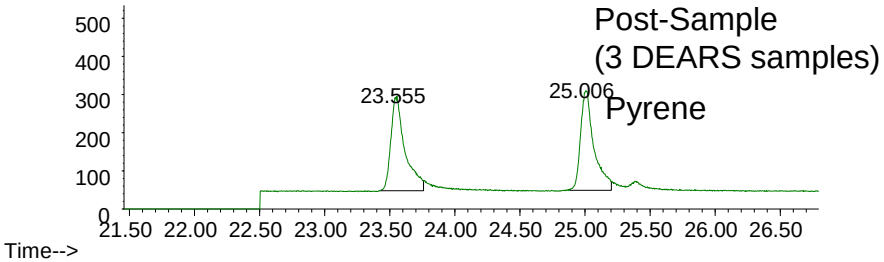



Method Detection Limits
pg/m3
4.00
3.00
2.00
1.00
0.00
0.72
0.57
0.55
0.72
0.68
1.42
1.11
0.57
3.04
3.26
Pyrene
Chrysene
Benzo[b]fluoranthene
Benzo[k]fluoranthene
Benzo[e]pyrene
Benzo[a]pyrene
Indeno[1,2,3-cd]pyrene
Benzo[ghi]perylene
Hopane
Norhopane

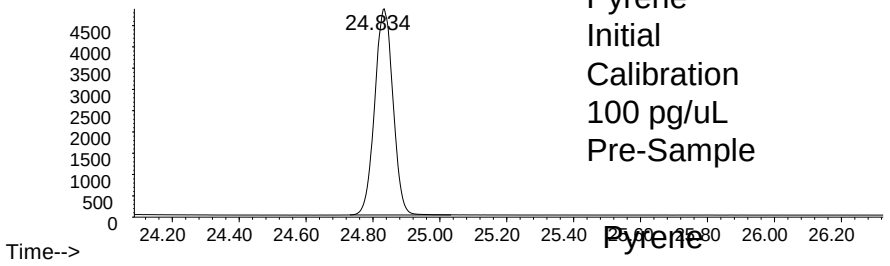

Average Conc./MDL
400
300
200
100
0
327
127
201
90
15
50
12
36
18
134
339
49
31
Benzo[b]fluoranthene3
Benzo[k]fluoranthene
Benzo[e]pyrene
Benzo[a]pyrene
Perylene
3-Methyl Chrysene
6-Methyl Chrysene 5
Dibenz[a,h]anthracene
Picene
Indeno[1,2,3-cd]pyrene
Benzo[g,h,i]perylene
Norhopane
Hopane
Compound

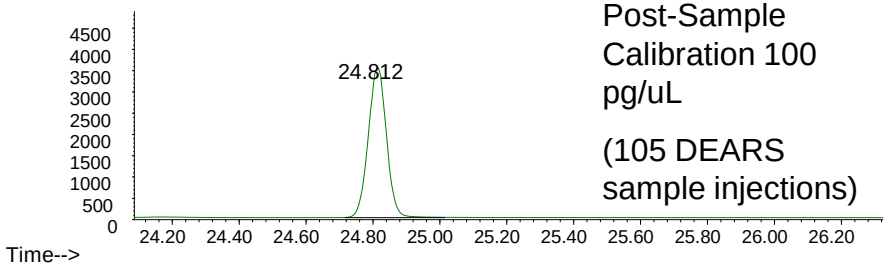
Initial Calibration vs. Post-Sample Comparison (SPE Cleanup)





(No SPE Cleanup)





LESSONS LEARNED

GCMS analysis without a cleanup or fractionation step is impractical for meeting typical Method 8270 QA requirement for PM sample analysis, especially at low concentrations

Sub-100 pg/m^3 concentrations are possible to measure for PAHs, but more difficult for other organic compounds with less prominent base peaks

Large Volume Injection could be further evaluated as an alternative to high volume sampling.

Disclaimer

The views expressed in this presentation are those of the authors and do not necessarily represent the views or policies of the U.S. Environmental Protection Agency.

Details:

S.R. McDow, M.A. Mazurek, M. Li, L. Alter, J. Graham, H.D. Felton, T. McKenna, C. Pietarinen, A. Leston, S. Bailey, S. Tong Argao, Speciation and atmospheric abundance of organic compounds in PM2.5 from the New York City area. I. Sampling network, sampler evaluation, molecular blank evaluation. *Aerosol Science & Technology* 42, 50-63, 2008.

J.M. Turlington, S.R. McDow, Solid phase extraction cleanup for non-polar molecular markers of PM2.5 sources. *Atmospheric Environment,* 44 2161-2165, 2010.

J.M. Turlington, S.R. McDow, Trueness, precision and detectability for sampling and analysis of organic species in airborne particulate matter. Analytical and Bioanalytical Chemistry 397, 2451-2463, 2010.